

THERMAL DECOMPOSITION OF TOBACCO IV. APPARENT CORRELATIONS BETWEEN THERMOGRAVIMETRIC DATA AND CERTAIN CONSTITUENTS IN SMOKE FROM CHEMICALLY-TREATED TOBACCOS¹

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Data from two groups of chemically-treated tobaccos reveal a contrast in their mode of thermal degradation and the composition of the smoke. Compared with untreated tobacco one group shows an increase in weight loss between 150 and 350°C (Zone A) and a decrease in weight loss between 350 and 500°C (Zone B). The smoke from these tobaccos also contains lower levels of TPM, phenol, and benzo[a]pyrene. The coal temperatures of cigarettes made from these treated tobaccos also are generally lower. The second group of treated tobaccos shows a decrease in weight loss in Zone A and an increase in weight loss in Zone B. The smoke from these tobaccos contains greater amounts of TPM, phenol, and benzo[a]pyrene. Furthermore, the coal temperatures of cigarettes made from these tobaccos are generally higher. It appears that each of these groups of treated tobaccos exhibits a different mode of thermal decomposition and that this results in differences in the composition of the smoke.

INTRODUCTION

In recent years much attention has been directed towards the production of cigarettes which yield reduced amounts of tar and nicotine. In addition, the selective reduction of various components in both the gas and particulate phases of cigarette smoke also has been emphasized.

Various approaches have been suggested for accomplishing these reductions (8, 10, 11). These include, for example, the breeding of tobacco varieties which yield lower amounts of undesirable smoke components, the extraction of tobacco with various solvents to remove possible precursors of these undesirable substances, the use of high porosity paper to lower particulate matter, the selective filtration of certain smoke components, and the alteration of the composition of cigarette smoke by chemically modifying the tobacco. This latter approach is currently being investigated in this laboratory.

In the previous paper (6) data were presented on

thermogravimetric analysis (TGA) of several chemically-treated tobaccos. It was found that the two major zones of thermal decomposition, 150-350°C and 350-500°C, were affected by these additives; and that on the basis of the weight losses in each zone, the treated tobaccos could be classified into nine groups. Analysis of the smoke from cigarettes made from two groups of these modified tobaccos revealed a correlation in the levels of certain smoke constituents and the thermogravimetric data. The purpose of this paper is to present in more detail this observed relationship.

EXPERIMENTAL

For each treatment a known amount of additive, exclusive of water of hydration was added to 800 grams of tobacco containing 12% moisture. In most cases an aqueous solution of the additive was applied as the tobacco was tumbled slowly in a rotating drum. The tobacco was alternately sprayed and dried (in warm air) to prevent it from being excessively wetted and to permit more even application of the additive. After being dried to a suitable moisture content the treated tobacco was sieved on a 2mm screen to remove the fines, and 85mm cigarettes were made using a Hauni-Baby cigarette making machine⁴.

Cigarettes to be smoked were selected on the basis of weight and pressure drop. These were equilibrated in a desiccator and the moisture content was determined. If required, sufficient water or a calculated amount of anhydrous CaSO₄ was placed in the desiccator to adjust the moisture content of the cigarette to 12%. Moisture was again determined and, if necessary, a second adjustment was made.

The cigarettes were smoked using a CSM-10 analytical smoking machine set to take a 35 ml puff of 2.0 seconds duration, one puff per minute. Total particulate matter (TPM) was determined as described by Ogg (7) except that the cigarettes were smoked to a 23mm butt length. The moisture in the particulate matter was determined gas chromatographically using Poropak Q (2). Temperature measurements were made using a 0.012 inch diameter Pt/Pt 13% Rh thermocouple as previously described (1). For these temperature determinations 10 cigarettes were smoked and the values averaged.

For the analysis of the smoke condensate at least 3 groups of 20 cigarettes each were smoked and the values obtained for each component were averaged. The smoking machine and the conditions employed are the same as described for the determination of

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⁴ Mention of a specific commercial product does not constitute endorsement by the United States Department of Agriculture or by the Kentucky Agricultural Experiment Station.

Table 1. Comparison of Thermogravimetric Data and Analytical Data on the Composition of Cigarette Smoke From Chemically-Treated Tobacco

	THERMAL DATA, TGA ¹		Nicotine mg	Phenol μg	SMOKE ANALYTICAL DATA ²				B[a]P ng	TPM, dry mg
	Zone A 150-350°C	Zone B 350-500°C			o-Cresol μg	m-,p-Cresol μg				
Untreated Tobacco	40.1 mg	32.9 mg	3.52 ±0.31	197 ±12	35.3 ±4.7	101 ±14			90.3 ±6.2	52.9 ±2.2
Group 6³	Ratios⁴				Ratios⁴					
NaNO ₂	1.13	0.50	0.43	0.60	0.44	0.38			0.53	0.36
NaNO ₃	1.13	0.73	0.37	0.65	0.60	0.35			0.66	0.37
KClO ₃	1.11	0.93	0.40	0.58	0.83	0.76			0.52	0.84
K ₂ CO ₃	1.06	0.85	1.0	0.79	1.2	1.3			1.0	0.62
Group 8³										
NaVO ₃ (5%)	0.95	1.21	0.46	1.3	1.3	1.2			1.5	0.94
NaVO ₃	0.83	1.23	0.58	2.1	2.9	2.1			1.5	0.69
NH ₄ VO ₃	0.87	1.28	0.44	1.8	1.9	1.5			3.6	0.74
Na ₂ B ₄ O ₇ ·H ₃ BO ₃ (7:3)	0.71	1.25	0.73	2.5	1.9	2.3			2.0	0.98

¹ 100 mg sample

² Per gram of tobacco burned.

³ 10% additive unless indicated otherwise

⁴ Values for $\frac{\text{weight loss of treated tobacco}}{\text{weight loss of untreated tobacco}}$ for TGA and $\frac{\text{level from treated tobacco}}{\text{level from untreated tobacco}}$ for smoke constituents.

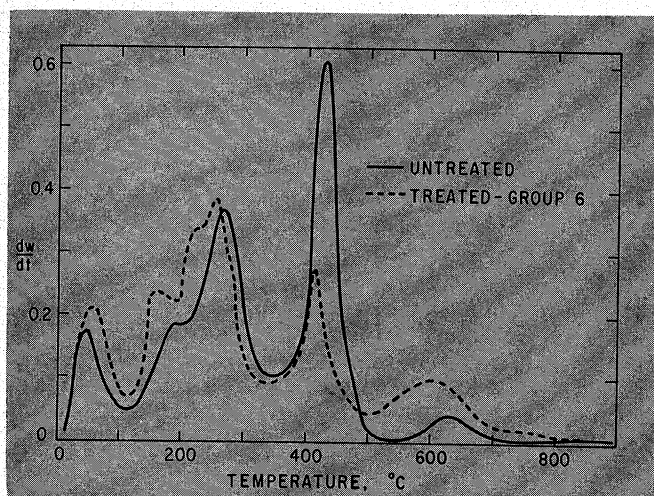


Figure 1—Derivative thermograms for untreated tobacco and tobacco treated with a representative additive from Group 6.

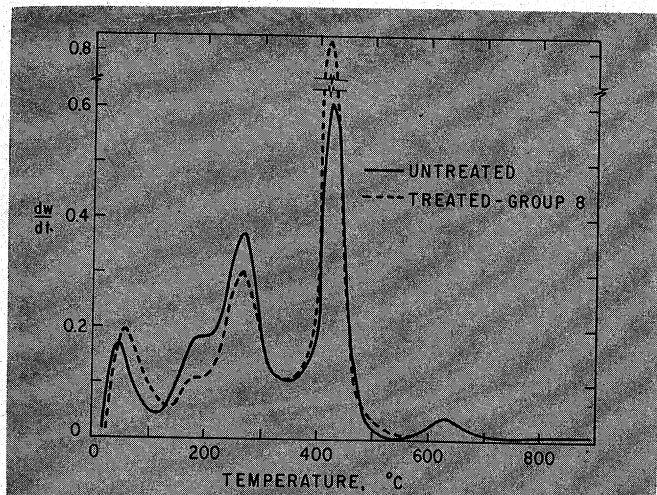


Figure 2—Derivative thermograms for untreated tobacco and tobacco treated with a representative additive from Group 8.

total particulate matter except that the condensates were collected in glass traps, packed with glass helices, and immersed in dry-ice acetone. Prior to smoking, aliquots of ¹⁴C-benzo[a]pyrene and sodium o-chlorophenoxide were added to the traps. These served as

internal standards to correct for losses during the work up and analysis of the condensate. The condensate was removed from the trap by alternate washings with cyclohexane and NaOH solution. After being partitioned into acidic, basic, and neutral fractions, the nicotine and phenols were determined as previously described (1). Benzo[a]pyrene was determined by fluorescence spectral analysis using isotope dilution to correct for losses (3).

RESULTS AND DISCUSSION

Derivative thermogravimetric curves (DTGA) for representative treated tobaccos from Group 6 and 8 together with the DTGA curve for untreated tobacco are shown respectively in Figures 1 and 2. These curves were obtained from thermogravimetric data as previously described (5). Comparing the curves for the treated tobaccos in Group 6 with the untreated tobacco reveals that the treated tobaccos have a higher rate of weight loss between 150 and 350°C (Zone A) and a lower rate between 350 and 500°C (Zone B) (Figure 1). In contrast, the treated tobaccos in Group 8 exhibit a lower rate of weight loss in Zone A and a higher rate in Zone B (Figure 2).

Data on the actual weight loss exhibited by the treated tobaccos in Zones A and B are presented in the first two columns in Table 1. For ease of comparison these data are presented as ratios of the weight loss exhibited by the treated tobaccos to that of the untreated tobacco. These ratios were obtained from data taken from the actual thermogravimetric curves and are corrected for any weight loss of additive. For the treated tobaccos in Group 6 the ratios reveal an increase in the weight loss in Zone A and a decrease in Zone B. In contrast, the ratios for the treated tobaccos in Group 8 show a decrease in the weight loss in Zone A and an increase in Zone B.

The levels of certain constituents in the smoke of the treated cigarettes also are shown in Table 1. As described above, these data also are presented as ratios. For the untreated tobacco the actual values plus standard deviations are shown. All data are based on a gram of tobacco burned and have been corrected for the moisture content of the cigarette and of weight of additive. These ratios reveal a decrease in the level of nicotine for each of the treated tobaccos except that treated with K₂CO₃. Comparison of these ratios to the ratios of the thermogravimetric

data for both groups of treated tobaccos reveals no apparent relationship. This is perhaps to be expected since nicotine is not pyrosynthesized but is volatilized from tobacco during burning. These ratios also show that tobacco treated with additives which form basic solution (K_2CO_3 and $Na_2B_4O_7 \cdot H_3BO_3$) yield the highest levels of nicotine. The reason for this probably is due to the "basic" additives releasing nicotine from "nicotine salts" in the leaf.

The ratios for phenol and the substituted phenols reveal that smoke from the Group 6 treated tobaccos generally contains less phenol, o-cresol, and m-p-cresol. An exception is the higher amounts of o-cresol and m-p-cresol in the smoke from the K_2CO_3 -treated tobacco. In contrast, smoke from the treated tobaccos in Group 8 contains higher amounts of phenol, o-cresol, and m-p-cresol. Particularly, noteworthy is the more than two-fold increase in the level of phenol in the smoke from the $Na_2B_4O_7 \cdot H_3BO_3$ -treated tobacco.

Comparing the levels of benzo[a]pyrene, it is seen that smoke from the treated tobaccos in Group 6 generally contains less benzo[a]pyrene than that from the untreated tobacco. Again an exception is the K_2CO_3 -treated tobacco where there is no change in the level of benzo[a]pyrene. In contrast, benzo[a]pyrene is much higher in smoke from the tobaccos in Group 8. For example, there is more than a three-fold increase in the level of benzo[a]pyrene in the smoke from the NH_4VO_3 -treated tobacco.

A possible explanation for the difference in the composition of the smoke from these two groups of treated tobaccos is indicated by the ratios of thermogravimetric data. These reveal that the treated tobaccos in Group 6 exhibit an increase in weight loss in Zone A and a decrease in Zone B, as has been previously reported, this weight loss in Zone A is due primarily to simple volatilization and pyrolysis (5). It is quite possible that the additives in Group 6 promote one or more of these processes either by reacting with the tobacco following treatment or as it is being heated. The loss of greater sample weight at lower temperatures in Zone A would therefore result in less material being available for combustion at the higher temperatures in Zone B. It is also possible that these additives may act to decrease the weight loss in Zone B in a manner which is unrelated to the decreased amount of material which is available for degradation in Zone B.

The ratios of the thermogravimetric data for the treated tobaccos in Group 8 reveals that there is a decrease in weight loss in Zone A and an increase in Zone B. It is thought that the greater amounts of phenol and benzo[a]pyrene in the smoke may be related, at least to some degree, to the greater quantity of tobacco undergoing degradation in Zone B. In addition, as vanadium salts promote certain high temperature oxidations. Additives containing vanadium oxides perhaps act as catalysts to promote the pyrosynthesis of the phenols and polynuclear aromatic hydrocarbons. As regards the effect of the sodium borate-boric acid mixture, one explanation may be that this additive reacts with certain precursors in the tobacco to form more thermally stable complexes which decompose at higher temperatures to form greater amounts of phenols. Studies to determine if this occurs are currently being undertaken in this laboratory.

Although no definite relationship is indicated between TPM and the thermogravimetric data, the treated tobaccos in Group 6 generally yield lower TPM than those in Group 8. An exception is the $KClO_3$ -

Table 2. Comparison of Cigarette Coal Temperatures and Thermal Data for Chemically-Treated Tobacco

	Coal Temperature °C	ΔWt^*	DTA**
Untreated Tobacco	713	32.9 mg	10.0 cm ²
Group 6		Ratios	
$NaNO_2$	686	0.50	0.42
$NaNO_3$	705	0.73	0.40
$KClO_3$	741	0.93	0.66
K_2CO_3	687	0.85	0.81
Group 8			
$NaVO_3$ (5%)	733	1.21	0.98
$NaVO_3$	733	1.23	1.0
NH_4VO_3	—	1.28	1.4
$Na_2B_4O_7 \cdot H_3BO_3$	718	1.25	1.0

* 100 mg sample

** 40 mg sample

treated tobacco which is rather high in TPM compared to the other tobaccos in this group. It is possible that the yield of TPM may be related to the rate of weight loss occurring in Zone B. This explanation is suggested because it is within this zone that tobacco ignites at approximately 410°C (5). Also, it has been found that rapid pyrolysis of organic materials produces more tar than slow combustion (4). Comparing the two groups of treated tobacco it is seen that those in Group 6 which, in general, yield lower TPM also exhibit a lower rate of weight loss in Zone B. (Figure 1). In contrast, the treated tobaccos in Group 8 yield greater TPM and show a higher rate of weight loss in Zone B (Figure 2). As there is no significant difference in pressure drop between the treated cigarettes and the controls this is not considered a factor in the observed changes in TPM and other smoke components.

Coal temperature measurements for the untreated and treated tobaccos are presented in Table 2. Since the thermocouple used in this work was made from 0.012 inch diameter wire the temperatures obtained are not absolute and are presented only to reflect relative differences (9). These values show that the coal temperatures of cigarettes in Group 6 generally are lower than the temperatures of cigarettes in Group 8. An obvious exception is the higher temperature of the $KClO_3$ -treated cigarettes which is thought to be due to the increase in oxygen concentration from the decomposition of the $KClO_3$. The ratios of weight losses occurring in Zone B together with the ratios of the peak areas of the corresponding exotherms also are presented in Table 2. These latter ratios were calculated from DTA data. Although there are certain exceptions, these data indicate that a relationship may exist between these parameters and the coal temperatures of the treated cigarettes. For example, these ratios are low (>1.0) for the Group 6 treated tobaccos which generally have lower coal temperatures than does the untreated cigarette. Conversely, the ratios for the Group 8 cigarettes which have higher coal temperatures are also higher (≤ 1.0).

SUMMARY

Data from two groups of chemically-treated tobaccos reveal a contrast in their mode of thermal degradation and the composition of the smoke. Compared with untreated tobacco one group shows an increase in weight loss between 150 and 350°C (Zone A) and a decrease in weight loss between 350 and 500°C (Zone B.) The smoke from these tobaccos also

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